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Influence of Sn on the magnetic ordering of Ni–Sn alloy synthesized using chemical reduction method

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ABSTRACT

The Ni–Sn alloy was synthesized using borohydride assisted chemical reduction method. The composition of the synthesized alloy was determined using atomic absorption spectroscopy which revealed that the observed composition of Sn is high when compared to the initial composition. The ultrafine particles are clearly observed from field emission scanning electron microscope for all the sample. The X-ray diffraction measurement confirmed that the as-synthesized samples are of amorphous like nature while the samples annealed at 773 K showed crystalline nature. The Fourier transform infrared spectroscopy confirmed metallic bond stretching in the alloy samples. The crystallization and phase transition temperature was observed from differential scanning calorimetry. The shift in the crystallization temperature of Ni with increasing percentage of Sn was observed. The vibrating sample magnetometer was employed to understand the magnetic behavior of the Ni–Sn alloy. As-synthesized alloy samples showed paramagnetic nature while the annealed ones exhibit the soft ferromagnetic, antiferromagnetic and paramagnetic nature. The saturation magnetization value and magnetic ordering in the Ni–Sn alloys depend on the percentage of Sn present in the alloy.

1. Introduction

The nickel based alloys find applications in various fields like, chemical, mechanical and electronic industries due to their corrosion and wear resistance. The Ni–Sn is one such kind of alloy with added applications like heat resistance, wettability, surface coating of electronic components, printed circuit board and in magnetic recording medium. The Ni–Sn alloy also have an important role in lithium ion batteries which is the most widely used power source in portable devices [1,2]. The Ni–Sn alloy forms the single phase (NiSn) at Sn-65:Ni-35 weight percentage composition. This phase is not thermodynamically stable as it does not appear in the phase diagram. The Ni–Sn alloy also have other stable intermediate phases like Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4. These intermediate phases are formed only after annealing above 300 °C. The physical and chemical properties of these intermediate phases are also similar to that of single phase [3–5].

Different methods are available on the literature for the preparation of nickel based alloys, the important methods are electrodeposition, chemical reduction, sputtering etc. The chemical reduction method has advantages like producing large quantity of ultra-fine alloy particles. The composition of the individual elements in the alloy can be easily controlled using chemical reduction method without much complication. The alloy prepared using chemical reduction method is suitable for compaction process, ferrofluids and magnetic memory systems [6]. The sodium borohydride is chosen as a reducing agent in chemical reduction method for the reduction of metal ions among the other reducing agents like hydrazine due to the following reason: (i) 1 mol of sodium borohydride is capable of producing 8 mol of electrons for reduction. (ii) This has a redox potential of − 1.24 V (iii) it can reduce metal ions in water, organic solvents medium with acidic, neutral and alkaline condition [7].

As there are large number of reports available on the synthesis and characterization of Ni–Sn alloy, only limited number of papers are available on the magnetic property of Ni–Sn alloy. In the present study attempts were made to prepare Ni–Sn alloy with different composition of Sn as 10%, 25%, 50% and 75% with respect to Ni and to study the effect of Sn constitution in the structural and magnetic property of nickel.

2. Experiment

Ni–Sn alloy was prepared using the chemicals, nickel(II) sulfate, tin(II) sulfate and sodium borohydride. All these chemicals were

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purchased from Merk India and used as received without any further treatment. In the preparation of Ni–Sn alloy, first the aqueous solution is prepared using nickel sulfate and tin sulfate salts. The molarity of tin sulfate was varied as 0.01 M, 0.025 M, 0.05 M and 0.075 M with respect to nickel sulfate so that the final molarity of the aqueous solution was 0.1 M. The capping agent poly vinyl pyrrolidone of 0.1 M was taken and dissolved in 50 ml of distilled water then added to the aqueous solution drop wise. This aqueous solution was kept under constant stirring for 30 minutes for the uniform distribution of nickel and tin ions. Then 0.5 M of sodium borohydride was taken in 50 ml of distilled water and added to the aqueous solution drop wise. When the pH of the aqueous solution reaches 10, black precipitate was observed which confirms the reduction of metal ions, then the solution was further stirred for 2 h to reduce all the metal ions present in the aqueous solution. The reduced black precipitate was collected and rinsed with distilled water for 6 times to remove the unwanted residues which may be formed while reducing metal ions and the reactants. Finally, the precipitate was washed with acetone and dried in room temperature [8]. The chemical reaction involved while reducing nickel and tin sulfate are given below.

$$NiSO_4 + 2\ NaBH_4 \rightarrow Ni + H_2 + B_2H_6 + Na_2SO_4$$

$$SnSO_4 + 2\ NaBH_4 \rightarrow Sn + H_2 + B_2H_6 + Na_2SO_4$$

The Ni–Sn alloys were prepared with the following percentage of nickel sulfate and tin sulfate precursor, (i) Ni-90:Sn-10 (Sample A), (ii) Ni-75:Sn-25 (Sample B), (iii) Ni-50:Sn-50 (Sample C) and (iv) Ni-25:Sn-75 (Sample D) along with this nickel and Sn were also prepared using the same procedure discussed above. All the prepared samples except tin was annealed in nitrogen atmosphere for 3 h at 773 K.

The quantitative analysis of nickel and tin in the alloy was done using atomic absorption spectroscopy (AAS – Perkin Elmer AAS 700). The surface morphology of the annealed samples were observed using field emission scanning electron microscopy (FE-SEM-FEI Quanta FEG 200). The structural information of both as-prepared and annealed samples were studied using powder X-ray diffraction (XRD-GE-XRD 3003 TT). Differential scanning calorimetry (DSC – Perkin Elmer Optima 5300 DV) was performed in nitrogen atmosphere to investigate the crystallization processes of the amorphous as-synthesized samples. The metallic bond stretching in the annealed samples were determined using Fourier transform infrared (FTIR – Perkin Elmer Spectrum) spectroscopy. The magnetic behavior of both as-synthesized and annealed samples were analysed by utilizing vibrating sample magnetometer (VSM – Lakeshore VSM 7410).

3. Result and discussion

3.1. Compositional analysis

The composition of individual constituent (nickel and tin) in the alloy is analysed using AAS. The relation between the initial composition and final composition of tin in the alloy is shown in Fig. 1 which also shows the expected composition of tin for comparison. From the figure, it is observed that in all the prepared alloy samples, reduction of tin is rich when compared to nickel and composition of tin is excess while comparing the initial composition. The excess of tin composition than the initial value in the alloy increases with increasing initial composition and reaches maximum for sample C then decreases for sample D. The reason behind this tin rich reduction is, the standard electrode potential of Ni ($E_0 = -0.25$ V) is less than the tin ($E_0 = -0.14$ V). This leads to the dominant reduction of tin than nickel [9,10].

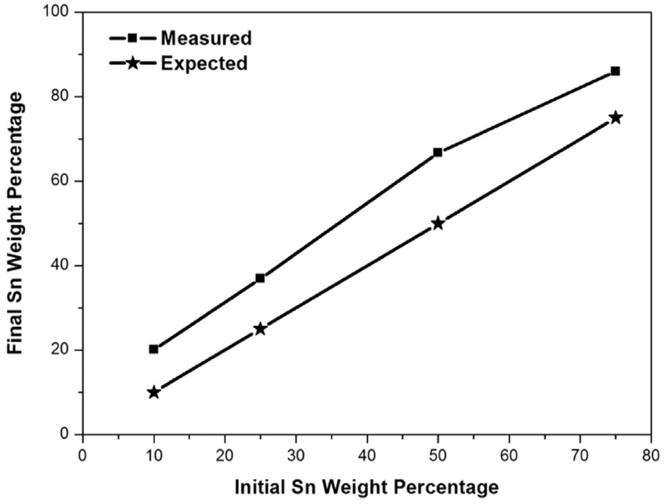

Fig. 1. Relationship between the initial and final value of tin percentage in the alloy.

3.2. Morphological nature

The surface morphology of the nickel, tin and alloy samples are observed using FESEM. The morphology of all the samples is shown in Fig. 2. The nickel shows the sheet or foam like nature while in the tin sample the particles are of uneven sized and shaped. The tin sample contains spherical, rod and agglomerated fine particles. FESEM image of sample A, shows that the fine particles are dispersed in foam with high agglomeration. The mixer of fine particles and foam are well observed in sample B, while the sample C shows the largely agglomerated fine particles. The morphology of sample D is spherical like nature with accumulation of large number of fine particles. This confirms that as the percentage of tin increases the morphology of the Ni–Sn alloy changes form foam like nature to ultrafine spherical like nature with agglomeration.

3.3. Structural analysis

The crystalline nature of both as-synthesized and annealed samples are examined using XRD. The XRD is measured with CuKα of wavelength 1.5406 Å in the scan range 20° to 80° with 0.04°/Sec step. The XRD pattern of as-synthesized tin, nickel and different composition of tin–nickel samples are shown in Fig. 3. The XRD pattern of as-synthesized tin shows the diffraction peaks corresponds to the 'd' values 2.90 Å, 2.78 Å, 2.06 Å, 2.01 Å, 1.66 Å, 1.48 Å, 1.46 Å and 1.44 Å which corresponds to the *hkl* planes (200), (101), (202), (211), (301), (112), (400) and (321) for metallic tin with reference to JCPDS file number 89-2958. The tin is in tetragonal structure with space group $I4_1/amd$. The XRD pattern of as-synthesized nickel, sample B and D show diffraction peaks with lower intensity. These diffraction peaks are correspond to nickel hydroxide and tin hydroxide.

The XRD pattern of annealed samples is shown in Fig. 4. The nickel sample shows the diffraction peaks with 'd' values 2.03 Å, 1.76 Å and 1.24 Å which corresponds to the *hkl* planes (111), (200) and (220) for metallic nickel phase with reference to JCPDS file number 04-0850. The nickel sample is in fcc structure with lattice parameter 3.52 Å and belongs to the space group Fm-3m. The XRD pattern of sample A also shows the nickel fcc phase with lattice parameter 3.54 Å. The increase in the lattice parameter is due to the substitution of tin atom in the place of nickel. In the case of